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One-Particle Self-Energy and the Virial Coefficients*

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The relation between the virial coefficients and the self-energy of the one-particle propagator is discussed for the "impurity" or Lorentz model. Expressions are derived for the equilibrium virial coefficients in terms of the self-energy parts describing the scattering of a particle due to clusters of one, two, three, etc., isolated impurities. In particular the second virial coefficient is expressed in terms of the t matrix describing the scattering due to one impurity. This expression is identical in form to that derived by Watson for a real gas. The expression is then reduced to a form involving the phase shifts. (If a bound state contribution exists, this can easily be included.) No assumption is made about the symmetry of the potential, and the result is a generalization of the Beth-Uhlenbeck-Gropper result for local spherically symmetric potentials. The model is also discussed classically.

I. INTRODUCTION

The impurity or Lorentz model, in which one considers a number of noninteracting particles in a large box which also contains a large number of randomly distributed scattering centers, has often been used for the theoretical study of *nonequilibrium* properties of gases and solids.[1-8] In particular, this model has recently been employed to study the divergences occurring in the density expansions of the transport properties of classical and quantum gases.[3-6]

In this paper we discuss the *equilibrium* properties for this model using the propagator technique of Edwards,[7] which has been used recently to show the divergences in the density expansion of the electrical resistivity.[4] There are two main purposes to the present paper. First, we indicate a new and comparatively simple approach to the quantum-mechanical equilibrium virial expansion problem, using the Lorentz model. This approach is through the self-energy of the one-particle propagator. It is planned to extend the method to include real gases. Secondly, since we use a method which has also been used to discuss the transport properties,[4] it should be possible to see more clearly why divergences occur in the one problem and not in the other. Some preliminary results concerning this question are given in the Appendix, (compare also Ref. 4).

In the next three sections, the quantum-mechanical virial expansion problem is set up and solved for the Lorentz model. The second virial coefficient is expressed in terms of the self-energy parts describing the interaction of a particle with one impurity. It is also expressed in terms of the t matrix for the scattering due to one impurity. (For simplicity, the absence of bound states is assumed.) The higher-order virial coefficients are related to the self-energy parts containing larger clusters of impurities, but the relations are more complicated.

For purposes of comparison with the quantum results, we give a classical discussion of the impurity model in Sec. 5.[9] For uncorrelated impurities, all the classical virial coefficients beyond the second vanish. In contrast, the higher-order quantum virial coefficients do not appear to vanish.

For spherical potentials, the second virial coefficient has been expressed in terms of the scattering phase shifts,[10,11] and also in terms of the scattering amplitude.[12] Baumgartl[13] has recently generalized the scattering amplitude expression to include scattering from noncentral and even nonlocal potentials. In Sec. 6, we derive a phase-shift formula which is valid for these more general potentials. Van Kranendonk,[14] by a different method, has previously given a partial generalization. His derivation is valid for "separable scattering problems" (see Sec. 6).

II. THE IMPURITY MODEL

The model consists of a number N' of noninteracting identical distinguishable particles in equilibrium at temperature T in a large box of volume Ω which also contains a large number $N\,(N \gg N')$ of randomly distributed scattering centers (impurities). To find the total free energy for the noninteracting particles, we calculate the free energy for one particle in the box and multiply the result by N'.

The one-particle Hamiltonian is

$$H = H_0 + V, \qquad (1)$$

where $H_0 = p^2/2m$ is the kinetic energy of the particle, and

$$V = \sum_{i=1}^{N} v_i \tag{2}$$

is the total potential energy due to the N impurities. $v_i = v(\vec{r} - \vec{R}_i)$ is the potential energy of the particle at $\vec{r}$ and the impurity at $\vec{R}_i$.

For a definite impurity configuration $\vec{R}^N \equiv \vec{R}_1 \cdots \vec{R}_N$, the partition function $Z = Z(\vec{R}^N)$ is given by

$$Z = \operatorname{Tr} e^{-\beta H} \tag{3}$$

with $\beta = 1/kT$. We shall not calculate the quantity (3). Instead, we set up a scheme for directly calculating $\overline{Z}$, the average value of Z, the average being taken over all configurations of impurities. The reason we can do this is discussed in the Appendix. There it is shown that, at least for the case of uncorrelated impurities, Z is a "self-averaging" quantity for a sufficiently large system. That is, for the overwhelming majority of impurity configurations, the deviation of Z from $\overline{Z}$ is negligible compared to $\overline{Z}$. Thus because the relative fluctuations in Z are negligible, and because $\overline{Z}$ is easier to calculate than Z, we shall calculate $\overline{Z}$.

The average $\overline{Z} = \langle Z \rangle_0$ is to be taken over all configurations according to

$$\langle Z \rangle_0 = \int \frac{d\vec{R}^N}{\Omega^N} Z(\vec{R}^N). \tag{4}$$

Occasionally we consider a more general (correlated) average, for which we use the notation

$$\langle Z \rangle = \int d\vec{R}^N P(\vec{R}^N)\, Z(\vec{R}^N), \tag{5}$$

where $P(\vec{R}^N)$ is the configurational distribution function for the impurities.

The free energy F and the pressure p are obtained from

$$F = -kT \ln \overline{Z}, \tag{6}$$

$$p = -\left(\frac{\partial F}{\partial \Omega}\right)_T . \tag{7}$$

Our aim is to calculate p as a power series in the density $n = N/\Omega$, in the limit $N \to \infty$, $\Omega \to \infty$ (n fixed).

III. CALCULATION OF THE PROPAGATOR

The partition function $\overline{Z}$ depends on the average propagator $\langle \exp(-\beta H) \rangle_0$. We introduce, now, the propagator in the "energy" language $G(z) = (z - H)^{-1}$ where z is complex. We have, of course, the relation

$$e^{-\beta H} = \mathcal{L}^{-1} G(z), \tag{8}$$

where $\mathcal{L}^{-1}$ denotes the inverse Laplace transformation

$$\mathcal{L}^{-1} G(z) = \frac{1}{2\pi i} \oint dz\, e^{-\beta z} G(z), \tag{9}$$

the contour to be taken counter clockwise and enclosing all the poles of $G(z)$, which occur at the eigenvalues of H.

We choose the contour to run arbitrarily close to the real axis, and assuming for simplicity that negative energy states are absent, we can write (9) as

$$\mathcal{L}^{-1} G(z) = -\frac{1}{\pi} \int_0^\infty dE\, e^{-\beta E} \times \frac{1}{2i} [G(E^+) - G(E^+)^\dagger], \tag{10}$$

where E is real and $E^+ \equiv E + i\epsilon$. From (3), (8), and (10) we obtain

$$Z = \mathcal{L}^{-1} \operatorname{Tr} G(z) = -\frac{1}{\pi} \int_0^\infty dE\, e^{-\beta E} \operatorname{Im} \operatorname{Tr} G(E^+) . \tag{11}$$

In order to calculate $\overline{Z}$, we must calculate $\overline{G}(E^+)$, the average propagator in the impurity system. If there are negative energy states, the contributions of the corresponding poles must be added to (10) and (11). We point out that the two limiting processes implicit in (11) must be taken in the order (1) $N \to \infty$, $\Omega \to \infty$ (N/Ω fixed), (2) $\epsilon \to 0$.

The propagator $G(z)$ satisfies the "integral equation"

$$G = G_0 + G_0 V G \tag{12}$$

with V given by (2). This equation can be iterated and averaged, and the resulting terms represented by diagrams following Edwards,[7] see Fig. 1. The only difference here is that the diagrams represent operators, so that attention must be paid to the order of the factors in a diagram. The contribution due to a given diagram can be written down by writing $\overline{G}$ for the arrowed double line, G_0 for an arrowed line, v_i for a broken line and N for each cross. As examples, we note that the fourth diagram on the right-hand side in Fig. 2 is equal to

$$N \langle G_0 v_1 G_0 v_1 G_0 \rangle_0 , \tag{13}$$

and the third diagram is equal to

$$N^2 \langle G_0 v_1 G_0 v_2 G_0 \rangle_0 . \tag{14}$$

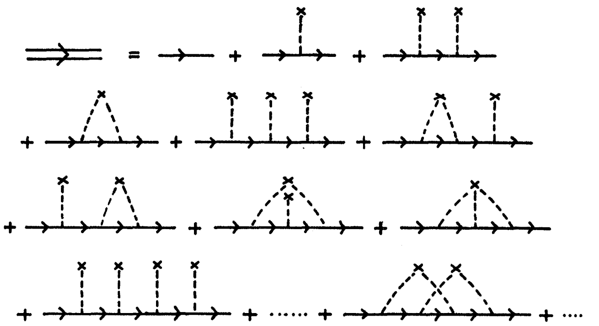

FIG. 1. Perturbation expansion for the average propagator.

The average in (13) is over all values of $\vec{R}_1$, and in (14) over all values of $\vec{R}_1$ and $\vec{R}_2$.

It is convenient to introduce Watson's transition operator[15] $T=T(z)$, defined by

$$T=V+VG_0T. \tag{15}$$

The propagator is expressed in terms of T by[16]

$$G=G_0+G_0TG_0\ . \tag{16}$$

The average propagator is therefore simply given by

$$\overline{G}=G_0+G_0\overline{T}G_0. \tag{17}$$

Note that $\overline{T}=\overline{T}(z)$ plays the role of a total or reducible self-energy, see Fig. 2. $\overline{T}$ is expressible in terms of the irreducible self-energy $\Sigma=\Sigma(z)$, see Fig. 3, in the usual way.[17] The irreducible self-energy diagrams are shown in Fig. 4. (An irreducible self-energy part cannot be broken into two parts by removing a G_0 line.) The diagrams for $\overline{T}$ are the same as those in Fig. 1 except that the first diagram is omitted, and the first and last G_0 lines are omitted in the other diagrams.

By rearranging the perturbation expansion for Σ as in Fig. 5, we see that Σ can be decomposed as

$$\Sigma=\Sigma_1+\Sigma_2+\cdots\ , \tag{18}$$

where Σ_1 contains those diagrams proportional to N, Σ_2 those proportional to N^2, etc. The series for $\overline{T}$ can be rearranged in the same way:

$$\overline{T}=\overline{T}_1+\overline{T}_2+\cdots\ . \tag{19}$$

From Figs. 2 and 3, the $\overline{T}_i$ and Σ_i are found to be related by

$$\overline{T}_1=\Sigma_1,\quad \overline{T}_2=\Sigma_2+\Sigma_1G_0\Sigma_1\ ,\quad \text{etc.} \tag{20}$$

By introducing the one-impurity t matrix t_i,

$$t_i=v_i+v_iG_0v_i+\cdots\ , \tag{21}$$

the diagrams containing repeated and uninterrupted interactions with the same impurity can be summed. By using a wiggly line for t_i, we obtain the series in Fig. 6. A similar diagram series for $\overline{T}$ can be written down. This diagram series can also be obtained from Watson's multiple scattering equation[15]

$$T=\sum_i t_i+\sum_{ij}{}' t_iG_0t_j+\sum_{ijk}{}' t_iG_0t_jG_0t_k+\cdots\ , \tag{22}$$

where the dashes on the summation signs indicate that consecutive indices must be different.

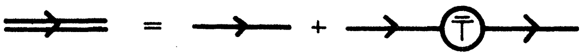

FIG. 2. The reducible self-energy T.

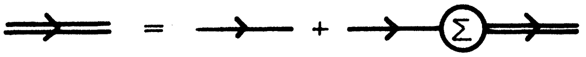

FIG. 3. The Dyson equation. Σ is the irreducible self-energy.

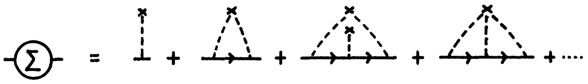

FIG. 4. Perturbation expansion for Σ.

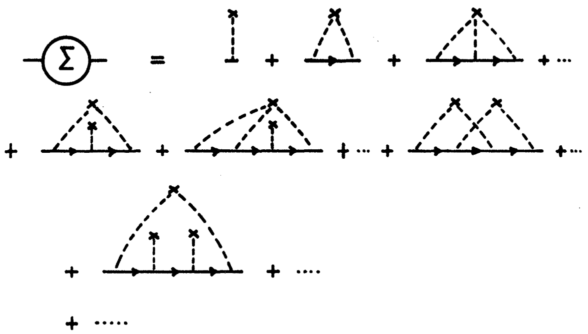

FIG. 5. Rearrangement of the perturbation series. The diagrams in the first line are proportional to N, those in the second line to N^2, etc.

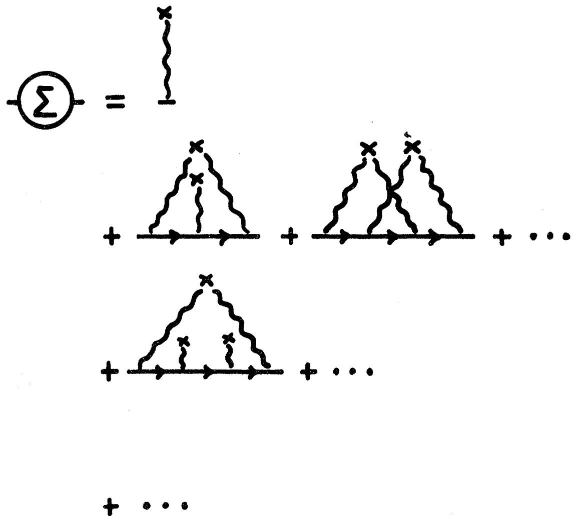

FIG. 6. Multiple scattering expansion for Σ.

IV. THE VIRIAL EXPANSION

From (11) we have

$$\bar{Z}/Z_0 = \frac{1}{Z_0}\,\mathcal{L}^{-1}\,\mathrm{Tr}\bar{G}(z)\,, \tag{23}$$

where $Z_0 = \Omega/\lambda^3$ is the partition function for the free particle, and $\lambda = h/(2\pi mkT)^{1/2}$ is the thermal wavelength of the particle. Substituting (17) into (23) and making use of the cyclic invariance of the trace we obtain

$$\bar{Z}/Z_0 = 1 + \frac{1}{Z_0}\,\mathcal{L}^{-1}\,\mathrm{Tr}G_0{}^2\bar{T}\,. \tag{24}$$

When the series (19) for $\bar{T}$ is substituted into (24), a density expansion of the form

$$\bar{Z}/Z_0 = 1 + a_1 n + \frac{a_2}{2!}\,n^2 + \cdots \tag{25}$$

results: The term involving $\bar{T}_1$ gives rise to the term in (25) linear in n, since $\bar{T}_1$ is proportional to N, and $Z_0{}^{-1}$ is proportional to Ω^{-1}. The other terms in (25) arise in a similar way. Further examples are discussed in the Appendix.

To calculate the free energy we need a density expansion for $\ln\bar{Z}/Z_0$,

$$\ln\bar{Z}/Z_0 = b_1 n + \frac{b_2}{2!}\,n^2 + \cdots\ . \tag{26}$$

Simple algebra gives for the b's

$$b_1 = a_1\,, \quad b_2 = a_2 - a_1{}^2\,, \quad \text{etc.} \tag{27}$$

From (6) we obtain

$$F - F_0 = -kT\left(b_1 n + \frac{b_2}{2!}\,n^2 + \cdots\right),$$

and from (7) we have

$$p - p_0 = kT\left(-b_1\frac{N}{\Omega^2} - b_2\frac{N^2}{\Omega^3} + \cdots\right),$$

or

$$p = p_0\,(1 - b_1 n - b_2 n^2 + \cdots)\,. \tag{28}$$

Comparison of (28) with the standard virial series

$$p\Omega = kT\,(1 + Bn + Cn^2 + \cdots) \tag{29}$$

shows that $B = -b_1$, $C = -b_2$, etc.

From (27) we see that a_1 and a_2 are needed for the second and third virial coefficients. We discuss here the evaluation of a_1, deferring the discussion of a_2 to a future publication. From (25), (19), and Fig. 5 we find that a_1 is given by

$$a_1 = \lambda^3\,\mathcal{L}^{-1}\,\mathrm{Tr}G_0{}^2\langle t_1\rangle_0\,. \tag{30}$$

By writing out the trace in the momentum representation, and using the relation (A.3) we find that the averaging over $\vec{R}_1$ in (30) can be omitted. The second virial coefficient $B = -a_1$ is therefore given by

$$B = -\lambda^3\mathcal{L}^{-1}\mathrm{Tr}G_0{}^2 t\,, \tag{31}$$

where t is the t matrix for the impurity at the origin. The form (31) for a real gas of identical molecules has been derived by Watson.[15] (Our B is a factor of 2 larger than Watson's because we are considering a mixture of two different types of particles.) By using the identity

$$G_1 = G_0 + G_0 t G_0\,,$$

where G_1 is the propagator with one impurity present, we find

$$\begin{aligned} B &= -\lambda^3\,\mathrm{Tr}\,\mathcal{L}^{-1}(G_1 - G_0) \\ &= -\lambda^3\,\mathrm{Tr}(e^{-\beta H_1} - e^{-\beta H_0}) \\ &= -\lambda^3(Z_1 - Z_0)\,, \end{aligned} \tag{32}$$

in an obvious notation. Equation (32) is the more familiar form for the second virial coefficient.[18]

In concluding this section we note from (27) and (30) that the second virial coefficient can be expressed in terms of the irreducible self-energy part Σ_1. It is interesting to speculate that the third virial coefficient might be expressible in terms of just Σ_2.

V. CLASSICAL DISCUSSION OF THE IMPURITY MODEL

In this section[9,19] we state the classical results analogous to the previous quantum results. The average classical partition function is

$$\overline{Z}/Z_0 = \frac{1}{\Omega}\int d\vec{r}\langle e^{-\beta V}\rangle , \tag{33}$$

where the integration is over all positions of the particle, and V is given by (2). For uncorrelated impurities a straightforward calculation gives

$$\overline{Z}/Z_0 = e^{-nB} , \tag{34}$$

$$\text{where } B = -\int d\vec{R}_1 (e^{-\beta v_1} - 1) . \tag{35}$$

Comparison of (34) with (26) shows that the only nonvanishing virial coefficient is the second, which is given by (35). [The reason for the apparent discrepancy of a factor of 2 in (35) is discussed following (31).]

The above results can be extended to include impurity correlations by using the Mayer classical diagram technique. The calculation exactly parallels the quantum calculations of the previous sections. When correlation is included, it is found that the second virial coefficient is still given by (35), and the third virial coefficient is given by

$$b_2 = \int\int d\vec{R}_1 d\vec{R}_2 [g(\vec{R}_1\vec{R}_2) - 1] f_1 f_2 , \tag{36}$$

where $f_1 = \exp(-\beta v_1) - 1$ is the Mayer cluster function, and $g(\vec{R}_1\vec{R}_2)$ is the impurity pair correlation function. Equation (36) shows explicitly that the third virial coefficient vanishes if the two impurities are uncorrelated, $g(\vec{R}_1\vec{R}_2) = 1$. The corresponding expression for a real gas

$$\int\int d\vec{R}_1 d\vec{R}_2 f_{12} f_{13} f_{23} ,$$

where $f_{12} = \exp(-\beta v_{12}) - 1$, also vanishes if there is no correlation between a pair of the three particles (e.g., $v_{12} = 0$).

The quantum third virial coefficient does not appear to vanish for uncorrelated impurities, and will be discussed further elsewhere.

VI. DERIVATION OF THE PHASE-SHIFT FORMULA FOR THE SECOND VIRIAL COEFFICIENT

From (31) we see that the second virial coefficient for the impurity model is proportional to the quantity

$$\alpha = \mathcal{L}^{-1}\,\mathrm{Tr}\,G_0(z)^2 t(z) . \tag{37}$$

The expression (37) is also correct for a real gas of molecules,[15] where one calculates G_0 and t for the relative motion of two molecules, using of course the reduced mass. The contribution of two-body bound states to (37) can easily be calculated, but we shall assume for simplicity that bound states are absent. For central potentials having no bound states Beth and Uhlenbeck[10] and Gropper[11] showed that α is given by

$$\alpha = \int_0^\infty dE\, e^{-\beta E}\,\frac{1}{\pi}\sum_l (2l+1)\frac{d\eta_l}{dE} , \tag{38}$$

where $\eta_l(E)$ is the phase shift experienced by the partial wave of angular momentum l, m, and energy E due to the scattering by the potential $v(r)$. Van Kranendonk[14] has generalized (38) to include all separable scattering problems (see the definition below). The result is

$$\alpha = \int_0^\infty dE\, e^{-\beta E}\,\frac{1}{\pi}\sum_\lambda \frac{d\eta_\lambda}{dE} , \tag{39}$$

where E, λ are the quantum numbers which diagonalize the S matrix. We refer to the paper of Van Kranendonk[14] for a discussion of earlier work on the problem, of possible applications of (39), and of the difficulty in trying to derive (39) by the method of Beth and Uhlenbeck, i.e., by treating the scattering problem as a boundary-value problem. The treatment of the problem in Ref. 13 has the advantage that the limit $\Omega \rightarrow \infty$, which is implicit in (37), can be carried out at the beginning, and the transition from the quasi-continuous to the continuous spectrum of scattering states does not give rise to any difficulties.

In this section we give a derivation of (39) which is valid for arbitrary (short-range) potentials. Our method is based on formal scattering theory, as is Van Kranendonk's, but is rather different and simple, and enjoys the same advantage, viz., the use of continuum normalization for the states.

To evaluate the trace in (37) we shall make use of a complete set of states furnished by the eigenvalue problem for H_0

$$H_0 | E\lambda\rangle = E | E\lambda\rangle , \tag{40}$$

where λ denotes a set of quantum numbers which completes the specification of the states. The states $|E\lambda\rangle$ belong to the continuous spectrum and are normalized according to

$$\langle E\lambda | E'\lambda'\rangle = \delta_{\lambda\lambda'}\,\delta(E - E') , \qquad \sum_\lambda \int_0^\infty dE\, | E\lambda\rangle\langle E\lambda | = 1 . \tag{41}$$

Since H_0 and the S-matrix commute, $[H_0, S] = 0$, we can choose the states $|E\lambda\rangle$ to be eigenstates also of S:

$$S | E\lambda\rangle = e^{2i\eta_\lambda(E)} | E\lambda\rangle , \tag{42}$$

where $\eta_\lambda(E)$ are the phase shifts. We recall for future use the relation (see, e.g., Ref. 14) between the matrix elements of t on the energy shell, and the phase shifts:

$$1-2\pi i\,\langle E\lambda\,|\,t(E^+)|\,E\lambda\rangle=e^{2i\eta_\lambda(E)}\;. \tag{43}$$

For so-called separable scattering problems,[14] one assumes that in addition to H_0, v is also diagonal in λ,

$$\langle E\lambda\,|\,v\,|\,E'\lambda'\rangle=\delta_{\lambda\lambda'}\langle E\lambda\,|\,v\,|\,E'\lambda\rangle\;. \tag{44}$$

We do not assume (44) in our derivation of (39).

Before writing out the trace we transform the operator $G_0{}^2t$ in the following way. From the Chew-Goldberger identity applied to the two-particle problem

$$t=v+vG_1v\;, \tag{45}$$

and the relations

$$vG_1=tG_0,\quad G_1v=G_0t, \tag{46}$$

we get

$$\frac{dt}{dz}=-vG_1{}^2v=-tG_0{}^2t\;,$$

and therefore

$$G_0{}^2t=-t^{-1}\frac{dt}{dz}\;. \tag{47}$$

Substituting (47) into (37) we get

$$\alpha=-\mathcal{L}^{-1}\mathrm{Tr}\,t^{-1}\frac{dt}{dz}=-\mathcal{L}^{-1}\mathrm{Tr}\frac{d}{dz}\ln t\;. \tag{48}$$

Carrying out the contour integration involved in $\mathcal{L}^{-1}$ in the same way as before [compare (9) and (10)] we get

$$\begin{aligned}\alpha&=\frac{1}{\pi}\int_0^\infty dE\,e^{-\beta E}\frac{d}{dE}\frac{1}{2i}\,\mathrm{Tr}[\ln t(E^+)-\ln t(E^-)]\\&=\frac{1}{\pi}\int_0^\infty dE\,e^{-\beta E}\frac{d}{dE}\frac{1}{2i}\,\mathrm{Tr}\ln t(E^+)t(E^+)^{\dagger-1}\;,\end{aligned} \tag{49}$$

where the fact that $t(E^-)=t(E^+)^\dagger$ has been used. [The fact that $\mathrm{Tr}(AB)=\mathrm{Tr}(BA)$ has been used in (48) and in (49).]

If (49) is to be identical to the phase-shift formula

$$\alpha=\frac{1}{\pi}\int_0^\infty dE\,e^{-\beta E}\frac{d}{dE}\sum_\lambda\eta_\lambda(E) \tag{50}$$

for all values of β, the expressions following the d/dE's in (49) and (50) must differ by at most a constant, i.e., we must have

$$\frac{1}{2i}\,\mathrm{Tr}\ln t(E^+)\,t(E^+)^{\dagger-1}=\sum_\lambda\eta_\lambda(E)+C\;, \tag{51}$$

where C is a constant independent of E.[20]

To establish the identity (51) we re-express the product $tt^{\dagger-1}$ as

$$tt^{\dagger-1}=1-2\pi it\delta(E-H_0) \tag{52}$$

which follows immediately from the unitarity condition

$$t-t^\dagger=-2\pi it\delta(E-H_0)t^\dagger\;. \tag{53}$$

[We use here the notation $t\equiv t(E^+)$.] The latter relation follows from (45) and repeated use of the identities

$$G(z)-G(z')=-(z-z')G(z)G(z') \tag{54}$$

and (46), together with

$$(E^+-H_0)^{-1}=\mathcal{P}/(E-H_0)-i\pi\delta(E-H_0).$$

From (52) we therefore have

$$\begin{aligned}\alpha(E)&\equiv\frac{1}{2i}\,\mathrm{Tr}\ln tt^{\dagger-1}\\&=\frac{1}{2i}\,\mathrm{Tr}\ln[1-2\pi it\delta(E-H_0)]\;.\end{aligned} \tag{55}$$

We now show that the trace in (55) is given by

$$\begin{aligned}&\mathrm{Tr}\ln[1-2\pi it(E^+)\delta(E-H_0)]\\&\quad=\sum_\lambda\ln[1-2\pi i\langle E\lambda\,|\,t(E^+)|\,E\lambda\rangle]\;.\end{aligned} \tag{56}$$

From the expansion

$$\ln(1+x)=x+a_2x^2+a_3x^3+\cdots$$

we have

$$\ln(1+\gamma t\delta)=\gamma t\delta+a_2\gamma^2t\delta t\delta+\cdots$$

and therefore

$$\begin{aligned}&\mathrm{Tr}\ln(1+\gamma t\delta)\\&\quad=\gamma\sum_{\lambda'}\int dE'\langle E'\lambda'\,|\,t(E^+)\delta(E-H_0)\,|\,E'\lambda'\rangle\\&\qquad+a_2\gamma^2\sum_{\lambda'\lambda''}\int dE'dE''\\&\qquad\times\langle E'\lambda'\,|\,t(E^+)\delta(E-H_0)|\,E''\lambda''\rangle\\&\qquad\times\langle E''\lambda''\,|\,t(E^+)\delta(E-H_0)|\,E'\lambda'\rangle+\cdots\;.\end{aligned}$$

Using the relation

$$\delta(E-H_0)|E'\lambda'\rangle=\delta(E-E')|E'\lambda'\rangle$$

and then carrying out the integrations over E', E'', etc., we obtain

$$\begin{aligned}\operatorname{Tr}\ln(1+\gamma t\delta)&=\gamma\sum_{\lambda'}\langle E\lambda'|t(E^+)|E\lambda'\rangle\\&\quad+a_2\gamma^2\sum_{\lambda'\lambda''}\langle E\lambda'|t(E^+)|E\lambda''\rangle\\&\quad\times\langle E\lambda''|t(E^+)|E\lambda'\rangle+\cdots.\end{aligned}\tag{57}$$

The matrix elements of $t(E^+)$ in (57) are all on the energy shell, where $t(E^+)$ must be diagonal in λ because S is [see (42)]. We can therefore do the sums over the intermediate state λ's, with the result

$$\begin{aligned}&\operatorname{Tr}\ln(1+\gamma t\delta)\\&\quad=\sum_{\lambda'}[\gamma\langle E\lambda'|t(E^+)|E\lambda'\rangle\\&\quad\quad+a_2\gamma^2\langle E\lambda'|t(E^+)|E\lambda'\rangle^2+\cdots]\\&\quad=\sum_{\lambda'}\ln[1+\gamma\langle E\lambda'|t(E^+)|E\lambda'\rangle],\end{aligned}\tag{58}$$

which establishes (56).

Substituting (43) into (56) and taking the logarithm we obtain

$$\alpha(E)=\frac{1}{2i}\sum_{\lambda}(2i\eta_\lambda+im2\pi)=\sum_{\lambda}\eta_\lambda+C,$$

where C is a constant independent of E. This completes the derivation of (51) and hence of the phase shift formula.

ACKNOWLEDGMENT

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APPENDIX

Fluctuations in Z

We show here that the relative fluctuations in Z vanish for an infinitely large system, at least for the case of uncorrelated impurities:

$$\langle(\Delta Z)^2\rangle_0/\bar{Z}^2=0,$$

where $\Delta Z=Z-\langle Z\rangle_0$ is the deviation from the average for a given configuration. Kohn and Luttinger[2] have described a large class of functions of the impurity configuration for which the relative fluctuations vanish. Rather than show that Z belongs to this class we shall give an explicit evaluation of a few typical diagrams corresponding to $\langle(\Delta Z)^2\rangle_0$. We show that

$$\langle(\Delta Z)^2\rangle_0/\bar{Z}^2=A/N,$$

where A is finite, and hence vanishes in the limit $N\to\infty$. The method is easily extended to the higher-order fluctuations such as $\langle Z^3\rangle_0-\langle Z\rangle_0^3$. In fact the nth order relative fluctuation is $O(N^{-n+1})$.

From the absence of relative fluctuations, it follows (see Ref. 2) that for the overwhelming majority of impurity configurations the deviation of Z from $\bar{Z}$ is negligible compared to $\bar{Z}$. It also follows that

$$\langle\ln Z\rangle_0=\ln\langle Z\rangle_0,$$

so that either of these quantities can be used in calculating the mean-free energy.

Consider now the second-order fluctuation term

$$\langle(\Delta Z)^2\rangle_0=\langle Z^2\rangle_0-\langle Z\rangle_0^2.\tag{A.1}$$

We substitute the expression

$$Z=\mathfrak{L}^{-1}\operatorname{Tr}(G_0+G_0TG_0)$$

for Z into (A.1). Writing out the traces in the momentum representation we obtain

$$\begin{aligned}\langle(\Delta Z)^2\rangle_0=\ &\mathfrak{L}_1^{-1}\mathfrak{L}_2^{-1}\sum_{\vec{k}_1}\sum_{\vec{k}_2}G_0(\vec{k}_1,z_1)^2G_0(\vec{k}_2,z_2)^2\\&\times[\langle T(\vec{k}_1,z_1)T(\vec{k}_2,z_2)\rangle_0\\&-\langle T(\vec{k}_1,z_1)\rangle_0\langle T(\vec{k}_2,z_2)\rangle_0],\end{aligned}\tag{A.2}$$

where

$$G(\vec{k},z)\equiv\langle\vec{k}|G(z)|\vec{k}\rangle,\quad T(\vec{k},z)\equiv\langle\vec{k}|T(z)|\vec{k}\rangle,$$

and $\mathfrak{L}_i^{-1}$ indicates an inverse Laplace transformation with respect to the variable z_i.

The multiple scattering expansion (22) can now be substituted into the expression

$$\langle T(\vec{k}_1,z_1)T(\vec{k}_2,z_2)\rangle_0$$

and the result represented by diagrams as in Sec. 3. The diagrams in $\langle T_1T_2\rangle_0$ are of two types, viz., those containing just self-energy insertions in the two one-particle propagators forming the two-particle propagator, and those containing interactions between these one-particle propagators. Typical self-energy diagrams are shown in Fig. 7. These diagrams are of the type $\langle T_1\rangle_0\langle T_2\rangle_0$, and as a result give no net contribution to (A.2). Typical interaction diagrams are shown in Fig. 8. We shall demonstrate that these diagrams are $O(1/N)$.

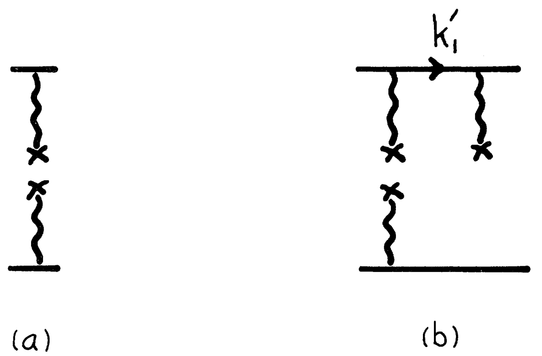

FIG. 7. Dressing of the two-particle propagator lines by self-energy insertions.

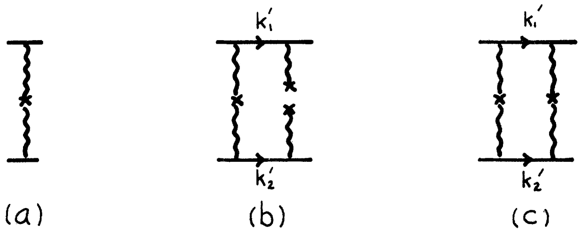

FIG. 8. Interaction parts for the two-particle propagator.

In writing down the contribution of a given diagram we use the relation

$$\langle\vec{k}|t_i|\vec{k}'\rangle = e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_i}\langle\vec{k}|t|\vec{k}'\rangle\,, \qquad (A.3)$$

where t is the t-matrix for $\vec{R}_i = 0$. Note that

$$\langle\vec{k}|t|\vec{k}'\rangle = \frac{1}{\Omega}\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, t(\vec{r})e^{ik'\cdot\vec{r}}$$

$$\equiv \frac{1}{\Omega} t_{\vec{k}\vec{k}'} \qquad (A.4)$$

contains the factor Ω^{-1}. $t(\vec{r})$ is the Schrödinger operator corresponding to t. We shall exhibit explicitly only the phase factors arising from (A.3), the volume factors from (A.4), and the factors of N, denoting the remaining factors by $f_1(\vec{k}_1\vec{k}_1{}'\cdots)$.

The diagram in Fig. 7(a) gives a contribution to $\langle T_1T_2\rangle_0$ equal to

$$\frac{1}{\Omega^2}N^2 f_1(\vec{k}_1)f_2(\vec{k}_2) = nf_1(\vec{k}_1)nf_2(\vec{k}_2)$$

which clearly is a term from $\langle T_1\rangle_0\langle T_2\rangle_0$. Figure 7(b) gives a contribution equal to

$$\frac{1}{\Omega^3}\sum_{\vec{k}_1{}'} N^3 f_1(\vec{k}_1\vec{k}_1{}')f_2(\vec{k}_2)$$

$$\times\left\langle e^{-i(\vec{k}_1-\vec{k}_1{}')\cdot\vec{R}_i} e^{-i(\vec{k}_1{}'-\vec{k}_1)\cdot R_j}\right\rangle_0$$

$$= (N/\Omega)^3\sum_{\vec{k}_1'} f_1(\vec{k}_1\vec{k}'_1)f_2(\vec{k}_2)\delta_{\vec{k}_1'\vec{k}_1}\delta_{\vec{k}_1\vec{k}_1'}$$

$$= n^2 f_1(\vec{k}_1\vec{k}_1)nf_2(\vec{k}_2)$$

which also cancels against a term in $\langle T_1\rangle_0\langle T_2\rangle_0$.

Figure 8(a) is equal to

$$\frac{1}{\Omega^2}Nf_1(\vec{k}_1)f_2(\vec{k}_2).$$

This quantity is $O(1/N)$. When the sums over $\vec{k}_1$ and $\vec{k}_2$ occurring in (A.2) are converted to integrals in the usual way,

$$\sum_{\vec{k}} \to \frac{\Omega}{(2\pi)^3}\int d\vec{k}\,,$$

this term becomes $O(N)$. Since $\bar{Z}^2$ is $O(N^2)$, the term in the relative fluctuation $\langle(\Delta Z)^2\rangle_0/\bar{Z}^2$ becomes $O(1/N)$, which is what we set out to prove.

Figure 8(b) is equal to

$$\frac{N^3}{\Omega^4}\sum_{\vec{k}_1'\vec{k}_2'} f_1(\vec{k}_1\vec{k}_1')f_2(\vec{k}_2\vec{k}_2')$$

$$\times\left\langle e^{-i(k_1-k_1')\cdot\vec{R}_i} e^{-i(\vec{k}_1{}'-\vec{k}_1)\cdot\vec{R}_j}\right.$$

$$\left.\times e^{-i(\vec{k}_2-\vec{k}_2{}')\cdot\vec{R}_i} e^{-i(\vec{k}_2'-\vec{k}_2)\cdot\vec{R}_l}\right\rangle_0$$

$$= \frac{N^3}{\Omega^4}\sum_{\vec{k}_1'\vec{k}_2'} f_1(\vec{k}_1\vec{k}_1')f_2(\vec{k}_2\vec{k}_2')$$

$$\times\delta_{\vec{k}_1-\vec{k}_1'+\vec{k}_2-\vec{k}_2',0}\,\delta_{\vec{k}_1'\vec{k}_1}\,\delta_{\vec{k}_2'\vec{k}_2}$$

$$= \frac{N^3}{\Omega^4} f_1(\vec{k}_1\vec{k}_1)f_2(\vec{k}_2\vec{k}_2)$$

and is $O(1/N)$. The same argument as that given above shows that this term gives a contribution $O(1/N)$ to the relative fluctuation.

Finally, Fig. 8(c) is equal to

$$\frac{N^2}{\Omega^4}\sum_{\vec{k}_1'\vec{k}_2'} f_1(\vec{k}_1\vec{k}_1')f_2(\vec{k}_2\vec{k}_2')$$

$$\times\left\langle e^{-i(\vec{k}_1-\vec{k}_1')\cdot\vec{R}_i} e^{-i(\vec{k}_1'-\vec{k}_1)\cdot\vec{R}_j}\right.$$

$$\left.\times e^{-i(\vec{k}_2-\vec{k}_2')\cdot\vec{R}_i} e^{-i(\vec{k}_2'-\vec{k}_2)\cdot\vec{R}_j}\right\rangle_0$$

$$= \frac{N^2}{\Omega^4} \sum_{\vec{k}_1'\vec{k}_2'} f_1(\vec{k}_1\vec{k}_1')f_2(\vec{k}_2\vec{k}_2')$$

$$\times \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_1'+\vec{k}_2'}$$

$$= \frac{N^2}{\Omega^4} \sum\nolimits_{\vec{k}_1'} f_1(\vec{k}_1\vec{k}_1')f_2(\vec{k}_2,\vec{k}_1+\vec{k}_2-\vec{k}_1')$$

$$= O(1/N)\,. \tag{A.5}$$

Again the same argument as that given above shows that this term gives a vanishing contribution to the relative fluctuation in Z.

Since Fig. 8(c) belongs to a class of diagrams (ladder diagrams) that individually give an infinite contribution to the zero-temperature electrical resistivity,[4] we shall examine the coefficient of N for the term in (A. 2) arising from (A. 5). Using the relation

$$G_0(\vec{k},z) = (z-\epsilon_{\vec{k}})^{-1}\,,$$

where $\epsilon_{\vec{k}} = \hbar^2k^2/2m$, we find that this coefficient is equal to

$$\frac{N}{\Omega^4}\oint\frac{dz_1}{2\pi i}\,e^{-\beta z_1}\oint\frac{dz_2}{2\pi i}\,e^{-\beta z_2}$$

$$\times\sum_{\vec{k}_1\vec{k}_2}\ \sum_{\vec{k}_1'\vec{k}_2'}\ \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_1'+\vec{k}_2'}$$

$$\times\frac{t_{\vec{k}_1\vec{k}_1'}(z_1)\,t_{\vec{k}_1'\vec{k}_1}(z_1)\,t_{\vec{k}_2\vec{k}_2'}(z_2)\,t_{\vec{k}_2'\vec{k}_2}(z_2)}{(z_1-\epsilon_{\vec{k}_1})^2(z_1-\epsilon_{\vec{k}_1'})(z_2-\epsilon_{\vec{k}_2})^2(z_2-\epsilon_{\vec{k}_2'})}\,. \tag{A.6}$$

To estimate (A. 6) we use the first Born approximation for the t matrices, $t_{\vec{k}\vec{k}'}(z) = v_{\vec{k}\vec{k}'}$, which is independent of z. We also assume for simplicity a potential of sufficiently short range that $v_{\vec{k}\vec{k}'}$ can be assumed to be independent of $\vec{k}$ and $\vec{k}'$. Converting the intermediate sums over $\vec{k}_1'$ and $\vec{k}_2'$ to integrals and carrying them out by contour integration we find that the resulting function diverges for $\vec{k}_2 = -\vec{k}_1$, $z_1 = E^+$, $z_2 = E^-$, in the limit $\epsilon \to 0$. This divergence is, however, integrable, and a finite result is obtained after integrating over z_1 and z_2. The integrals over z_1 and z_2 are not present in Neal's expression[4] for the zero-temperature resistivity and this is the reason for the divergence he obtains for the ladder diagram contributions.

The finiteness of (A. 6) can be seen more simply by carrying out the z integrations before the $\vec{k}'$ integrations. The residues from the poles at $\epsilon_{\vec{k}_1}$, $\epsilon_{\vec{k}_1'}$, etc., are clearly finite and remain finite even when $\vec{k}_2 = -\vec{k}_1$. A similar analysis can be carried out for the higher-order ladder diagrams.

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[9] Since the completion of the present work, the paper of Burke and Lebowitz has appeared (see Ref. 19), which contains the main results of this section. We therefore give only a brief summary in this section.

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[20] The constant C in (51) can be evaluated *a priori* in the following way. Consider the limiting case $E \to \infty$. The left hand side involves $\ln vv^{-1} = 0$. From (43), it follows from the reality of $\langle E\lambda|v|E\lambda\rangle$ that, in the limit $E\to\infty$, $\eta_\lambda(E)$ approaches the value $\eta_\lambda = m\pi$, where m is an integer, so that $C = -\Sigma_\lambda m\pi$. Conventionally one chooses $m = 0$, and with this choice $C = 0$.